Fe_3C. The low thermal stability of the carbonyl prevents a Curie point determination which would clearly establish the nature of the ferromagnetic impurity. If, however, we assume that the impurity is metallic iron, we may estimate the amount of iron necessary to give the observed ferromagnetism. The specific magnetization of pure iron is about 216.[7] The observed specific magnetization of the carbonyl is 6×10^{-8}. The fraction of metallic iron present as impurity is $6 \times 10^{-8}/216$ or about 0.003% by weight. Under the conditions of the magnetic measurements in the dark, at room temperature, the iron concentration is increasing at such a rate that it would become twice as great in about eighty days.

The susceptibility of the pure carbonyl was estimated as -0.07×10^{-6} but from this must be subtracted algebraically the *paramagnetism* of the iron impurity. There is no easy way of obtaining the paramagnetism of metallic iron at room temperature but from Stern-Gerlach experiments and from the known susceptibility of metallic manganese we may estimate the paramagnetic susceptibility of iron as certainly not much over 10^{-4}. A fraction of iron amounting to 0.003% would then contribute only 3×10^{-9} unit of susceptibility, which is negligible compared with an observed susceptibility for the carbonyl of about 70×10^{-9}.

It may, therefore, be concluded that the diamagnetic susceptibility of iron tetracarbonyl is, while rather small, nevertheless normal. The small magnitude of the susceptibility may be due to paramagnetic impurities, such as γ-Fe_2O_3 for which no good test is available. A second possible explanation is the presence of a rather large temperature independent paramagnetism.

Summary

The magnetic susceptibility of iron tetracarbonyl at room temperature, corrected for ferromagnetic impurity, is -0.07×10^{-6}. The carbonyl appears to undergo a slow change, with an increase in susceptibility, when it stands in the dark.

EVANSTON, ILLINOIS RECEIVED SEPTEMBER 29, 1943

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[7] International Critical Tables, Vol. VI, p. 376.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF LAWRENCE COLLEGE AND OF INDIANA UNIVERSITY]

The Surface Tensions and Parachors of the Methyl and Ethyl Amines

BY ELIJAH SWIFT, JR., AND C. RICHARD CALKINS[1]

A comparison of the boiling points of the methylamines and freezing points of the ethylamines is somewhat surprising. The boiling points of the methylamines are reported as -6.79,[2] $+6.9$,[3] and $+3.2°$,[4] and the freezing points of the three ethylamines as -83.8,[5] -50,[6] and $-114.8°$.[7,8]

Having on hand carefully purified samples of these compounds, measurements of the surface tensions were undertaken with the hope that if the lower values for the tertiary amines were caused by structural abnormalities of the liquids, this might show up in the parachor values.

Purification of Materials.—The three ethylamines and the di- and trimethylamine were samples whose purification has been described previously.[9] In addition each sample used was dried over potassium hydroxide or with sodium fluorenone[10] in the absence of air and distilled in vacuum, a second slow evaporation without spattering then being made directly into the evacuated apparatus.

A second sample of diethylamine was prepared by another method. Eastman Kodak Co. diethylamine hydrochloride was treated with potassium nitrite and hydrochloric acid and the resulting nitroso compound washed with distilled water and steam distilled. It was then treated with tin and hydrochloric acid and reduced to the amine hydrochloride, which was made alkaline with potassium hydroxide to drive out the amine. The purified compound was twice fractionated in a 30-cm. packed column. The boiling point (uncor.) was 55° and no change in this temperature was observed during the distillation of the accepted fraction. The product was dried over potassium hydroxide and twice distilled *in vacuo*, leaving no visible residue.

For the preparation of the methylamine,[11] Eastman Kodak Co. methylamine hydrochloride was extracted with pure dry chloroform for thirty hours to remove higher amines, then recrystallized from absolute alcohol and extracted for an additional twenty hours with chloroform. The resulting product was treated with excess potassium hydroxide and the gaseous methylamine passed over potassium hydroxide and yellow mercuric oxide to remove any traces of ammonia. The amine was liquefied with dry-ice and ether, desiccated by dissolving sodium fluorenone in it and then distilled into the evacuated apparatus.

Method of Measurement.—The surface tensions of the compounds were measured by the capillary rise method in the capillarimeter sketched in Fig. 1. About 20 ml. of the pure amine was distilled in through A, which was then sealed off. Sufficient amine was poured into B, by tilting the apparatus, so that the level of the liquid in the capillary just reached point C, indicated by a small scratch on the tube. The liquid meniscus was always brought

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[1] Present address, Institute of Paper Chemistry, Appleton, Wis.

[2] W. A. Felsing and A. R. Thomas, *Ind. Eng. Chem.*, **21**, 1269 (1929).

[3] A. Simon and J. Huter, *Z. Elektrochem.*, **41**, 28 (1935).

[4] H. W. Thompson and J. W. Linnett, *Trans. Faraday Soc.*, **32**, 681 (1936).

[5] "International Critical Tables," McGraw-Hill Publishing Co., New York, N. Y., 1928.

[6] A. W. Hofmann, *Ber.*, **22**, 705 (1889).

[7] J. Timmermans, *Chem. Zentr.*, **85**, I, 618 (1914).

[8] There is considerable disagreement on the exact values of these freezing points. However, diethylamine is the only one of the three which can be frozen with ether-dry-ice mixtures.

[9] E. Swift, Jr., THIS JOURNAL, **64**, 115 (1942).

[10] H. E. Bent and H. M. Irwin, *ibid.*, **58**, 2072 (1936).

[11] B. A. Kelso and W. A. Felsing, *ibid.*, **60**, 1949 (1938).

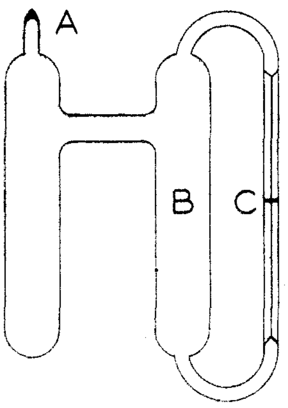

Fig. 1.

within 0.3 mm. of this point to avoid variations in the diameter of the capillary.[12]

For most of the measurements, the height of rise was measured with a Gaertner cathetometer[13] reading to 0.05 mm. Between readings, the apparatus was tilted to make sure that the walls of the capillary were thoroughly wet, and a fresh surface was formed during each series of measurements by pouring an excess of liquid into the space above the capillary and letting it flush out the capillary. Six to twelve measurements were made at each temperature, the extreme variation among measurements being usually less than 0.2 mm. At least two samples of each compound were measured.

The temperature was maintained to ±0.03° in a thermostat with a plate glass front. A thermometer calibrated against a Bureau of Standards calibrated thermometer was used for the 15 and 25° points and a second thermometer checked against the first and at the sodium sulfate transition point was used for the 35° point. The temperature as reported was probably within 0.05° of the true temperature.

The capillarimeter was calibrated with benzene[5] and with ether.[5] Eastman Kodak Co. anhydrous ether after standing over calcium chloride was distilled from phosphorus pentoxide and the middle fraction taken. This was desiccated with sodium fluorenone[10] and distilled into the evacuated apparatus. The benzene used was thiophene-free A. R. grade and was distilled from sodium in one case and from phosphorus pentoxide in the second case. The mean of six values of the radius of the capillary obtained using benzene agrees well within the limits of error with the mean of three values obtained using ether. The correction for the weight of the liquid in the meniscus[14] was applied although it was found to be within the limits of experimental error. The precision of measurement is estimated to be about 0.2% and the over-all accuracy about 0.5%, the values for dimethylamine and trimethylamine being the least accurate of the group.

Results.—The values obtained for the surface tensions of the liquids at the equilibrium vapor pressure of each are summarized in Table I. The only other values in the literature in this temperature range are those of Jaeger[15] who used the method of maximum bubble pressure. Values interpolated from his tables for diethyl- and triethylamine range 5–10% lower than those found in this investigation. Because of this discrepancy considerable pains were taken to check the values found for one of these compounds. Two of the samples of diethylamine used were repeatedly frozen while pumping under high vacuum. They were then carefully distilled in a closed system into the apparatus. A fourth, entirely new, sample was prepared by another method (see "Purification of Materials"). No difference in surface tension among any of these samples was observed.

TABLE I

SURFACE TENSIONS IN DYNES PER CENTIMETER AND PARACHORS

	15°	25°	35°	*P* calcd.	*P* obs.	Calcd. – obs.
Methylamine	20.6_0	19.1_9	17.6_5	100.7	99.7	1.0
Dimethylamine	17.6_1	16.3_3	15.0_8	140.3	140.3	0
Trimethylamine	14.5_3	13.4_7	12.2_4	179.9	182.5	−2.7
Ethylamine	20.5_6	19.2_1	17.8_2	140.3	139.9	0.4
Diethylamine	20.6_3	19.3_9	18.2_0	219.5	219.8	−0.3
Triethylamine	21.1_2	20.0_5	18.9_8	298.7	296.4	2.3

The somewhat lower boiling or freezing points of the tertiary amines might be ascribed to hydrogen bonding which can take place in the case of the primary and secondary amines but not in the tertiary amines. If there is any great amount of hydrogen bonding this might be expected to show up in the parachor values as considerable negative deviations.[16]

The parachors for the compounds were calculated at all three temperatures using density and vapor pressure values cited in reference 9. The maximum variation in parachor value between 15 and 35° for any one compound was 0.6 parachor unit, and was judged not to be significant. The average values of the parachors are shown in the table. These are compared with the values calculated using the atomic parachors[17] N = 12.5, C = 7.2 and H = 16.2. It seems doubtful if any significance can be ascribed to the differences, which are of the usual order of magnitude, especially in view of the fact that the calculated values may be made to vary by more than these differences by selecting other values of the parachors for C and H.[18] The lack of any significant deviation is confirmed by other work[19] which indicates that the amount of hydrogen bonding in amines is extremely small near room temperature. Pauling[20] has estimated that the strength of the N · · · H–N bond is about 1.6 kcal. in these compounds, so that hydrogen bond formation could be of little importance at the boiling points of the methylamines although it might assume slight importance at temperatures as low as the freezing points of the ethylamines.

Curtiss and Hirschfelder[21] have very tentatively estimated the amount of hydrogen bonding in the gas phase for methylamine and dimethylamine to be 4–5 mole per cent. ("instantaneously formed double molecules"). This would point to an even greater degree of association in the liquid phase which seems unlikely in view of the present evidence.

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(12) In one determination with trimethylamine where the sample was too small to bring the meniscus to the mark, the result was weighted less in the calculations.

(13) Catalog number M908.

(14) T. W. Richards and E. K. Carver, THIS JOURNAL, **43**, 827 (1921).

(15) F. M. Jaeger, *Z. anorg. Chem.*, **101**, 1 (1917).

(16) S. Sugden, "The Parachor and Valency," Routledge, London, 1930, p. 169 ff.

(17) S. Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., New York, N. Y. 1940, p. 516.

(18) See, for example, the various values given by N. S. Bayliss, THIS JOURNAL, **59**, 444 (1937).

(19) W. D. Kumler, *ibid.*, **57**, 600 (1935).

(20) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

(21) C. F. Curtiss and J. O. Hirschfelder, *J. Chem. Phys.*, **10**, 491 (1942).

The most important factor affecting the boiling points of these compounds is probably the dipole moment. Smyth[22] gives for the dipole moments of the three methylamines values of 1.23, 0.96 and 0.6, the more symmetrical amine having the lower amount. Trimethylamine, being the least firmly bound by dipole forces, therefore shows the lowest surface tension and can be more readily evaporated from the surface than would be expected on the basis of its molecular weight alone. The differences in the dipole moments of the three ethylamines is less pronounced, so that the effect of adding an ethyl group to the molecule predominates over the slight decrease in dipole moment and the boiling points fall in the normal order.

The authors wish to thank the Institute of Paper Chemistry for the loan of a cathetometer used in part of this investigation, and the Research Fund of the Graduate School of Indiana University for a grant.

Summary

1. The surface tensions of the methyl and ethylamines have been measured at 15, 25 and 35° with an accuracy of 0.5%.

2. The parachors do not indicate any structural abnormalities in the liquid state.

BLOOMINGTON, INDIANA RECEIVED AUGUST 20, 1943

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[22] C. P. Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Company, New York, N. Y., 1931.

[CONTRIBUTION FROM THE PHILLIPS PETROLEUM COMPANY, RESEARCH DEPARTMENT]

The Reaction of Sulfur Dioxide with Olefins: the Ceiling Temperature Phenomenon

BY R. D. SNOW[1a] AND F. E. FREY

The liquid phase reaction of monolefins with sulfur dioxide to form polysulfones can be brought about by means of soluble catalysts, such as oxygen, peroxides, alkali nitrates, etc., or by exposure to actinic light.[1b] In the total absence of both light and catalysts apparently no reaction occurs.

In the course of an experimental study of this reaction embracing a variety of olefins and catalytic agencies, the reaction has been found, under certain conditions, to exhibit a steep negative temperature coefficient of rate. Raising the temperature through a few degrees, while maintaining a homogeneous liquid condition, suffices to virtually arrest reaction.

At the upper limiting temperature, or "ceiling temperature," the reaction between sulfur dioxide and some olefins was started or stopped repeatedly at will by alternately lowering and raising the temperature through an interval of one or two degrees. The ceiling temperatures found for the cases studied were as follows: propylene 87–89°, isobutylene 4–5°, 1-butene 63–66°, and 2-butene (*cis–trans* mixture) 43–45°. No change in the ceiling temperature was detected from start to completion of conversion in any experiment. Over a wide range of initial proportions of sulfur dioxide and a given olefin, the ceiling temperature was found to be independent of the relative concentration of the reactants. To our knowledge, no such sharp ceiling temperature effect has ever been reported for a homogeneous strictly chemical reaction. The closest analogy is found in the processes of photosynthesis and fermentation, both of which involve living cells.

Experimental Part

Since the temperature effect may be due to an unusual inhibition, pains were taken to prepare olefin reactants in high purity. The sulfur dioxide was the extra dry refrigerating grade. The Pyrex glass reaction tubes used were carefully cleaned, and reactant transfers were made in a vacuum system.

Isobutylene.—This olefin was selected as being particularly well suited for observing the ceiling temperature effect, since it did not react at room temperature, and when it did react it gave a heteropolymeric sulfone which was insoluble in sulfur dioxide and was easily observed by inspection. Three tubes were prepared. To one was added 1 cc. of 5% alcoholic lithium nitrate solution and to another the 3% hydrogen peroxide–paraldehyde–alcohol mixture used by Marvel.[2] The third tube was sealed without a catalyst (or alcohol addition) to study the photochemical reaction. A small quantity of resin (2–4%) formed in the tubes containing catalysts during the warming to room temperature after filling, but the reaction stopped well below room temperature; the solution cleared and no further resin formed during several hours. The tubes containing catalysts were then cooled slowly in a water-bath. The reaction in both started at +3.5–4° and was stopped at will by warming to 6°. The process of starting and stopping the reaction by alternately cooling and warming to these temperature levels was repeated several times during which possibly 20% conversion was obtained. During this time, the hydrogen peroxide catalyst became inactive and no further reaction occurred, even as low as 0°. The tube containing no catalyst was handled in a similar way. It was first exposed to bright sunlight at room temperature and no resin formed. On cooling slowly in the sunlight in a water-bath in a clear vacuum bottle, the resin formation began at about 4°, and took place quite rapidly at 3°. Once the mixture became cloudy, however, the reaction was slowed down by the screening of the light by the suspended resin. Here again, the reaction could be stopped by raising the temperature to 6° and started by cooling to 3.5–4°. All three tubes were then placed in a refrigerator and maintained at 8.5 to 9.5° for thirty-six hours, to see whether a slow reaction would occur slightly above the ceiling temperature. No additional resin formation could be detected. The tube containing lithium nitrate was again cooled, and the reaction began at 4°. After repeating the observation several times, the reaction

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[1a] Lt. Col. with Chemical Warfare, Edgewood Arsenal, Md.

[1b] For a more complete general discussion of the reaction and references to prior literature, see Frey and Snow, *Ind. Eng. Chem.*, **30**, 176 (1938).

[2] Marvel, THIS JOURNAL, **57**, 2312 (1935).